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(54) SURFACE-ACTIVE OXYALKYLATED AMINES

(71) We, TEXACO DEVELOPMENT CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 135 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The field of this invention relates to the production of new surfactant compounds. Surfactant compounds have long been prepared by the addition of ethylene oxide to compounds having labile hydrogen atoms which will open the epoxide ring to form an addition product with such materials. One class of such compounds which have been reacted with alkylene oxides to produce surfactants and other compositions are compounds having a primary amine group in a terminal position. For example, U.S. Patent 3,352,916 describes the addition of alkylene oxide groups to amino hydrogen atoms of fatty amine derivatives of fatty acids. This patent discloses, however, the amination of the terminal hydroxyl groups resulting from the addition of the ethylene oxide.

Further, U.S. Patent 3,891,709 describes a polyoxyalkylene amine wherein a compound having a terminal amine group is reacted with the alkylene oxide to produce an anti-static agent. The compound having a basic amino terminal group is derived from the reaction of a long chain epoxide with an alkanolamine such as diethanolamine or diisopropanolamine. This results in an ether linkage between the moiety carrying the nitrogen atom and the hydrocarbon residue of the epoxide used in the reaction. Usually there exists a hydroxyl group on the beta carbon atom. Anti-static agents for polyolefins have been described in the art discussed in U.S. Patent 3,891,709 which have the following formula:

$$R'_1-O-CH_2-CH_2-CH_2-N\begin{matrix}R'_2\\R'_3\end{matrix}$$

wherein R'_1 is an alkyl, alkenyl, alkylcycloalkyl, aryl, alkylaryl or alkenylaryl group containing 6 to 25 carbon atoms in the alkyl or alkenyl moiety, and R'_2 and R'_3 each is hydrogen, an alkyl group having 1 to 5 carbon atoms or a radical $(C_mH_{2m}O)_nH$ in which m is 2 or 3 and n is an integer of 1 to 10.

While there are many surface-active agents known in the art, there is still need for reduced wetting times and greater reduction of surface tension of aqueous materials not provided by such known prior art compounds.

Additional surface-active agents are known from U.S. Patents 2,508,036; 3,031,510; and, many others.

This invention provides surface-active agents having greatly reduced wetting times in aqueous solutions and other improved surfactant properties which are represented by the formula:

$$R-(OCH_2CH)_xOCH_2CH-N\begin{matrix}(CH_2CH_2O)_yH\\(CH_2CH_2O)_zH\end{matrix}$$
$$\qquad\quad CH_3 \qquad\quad CH_3$$

where R is an alkyl group having from 8 to 18 carbon atoms, preferably 10 to 14 carbon

atoms. x has an average value of from 0 to 4, preferably 0.5 to 1.5, and y and z have an average value of from two to 20, preferably from 5 to 15, provided that y and z are each at least one.

The above compounds provide dramatically lower wetting times than prior art amine ethoxylates as well as lower pour points and reduced surface tension in aqueous systems.

Generally, these materials are prepared by reacting ethylene oxide with an aminated propylene oxide adduct of a long chain alcohol.

The surface-active compounds of this invention are represented by the foregoing formula. These compounds are prepared generally from long chain, usually linear, alcohols having from 8 to 18 carbon atoms by propoxylating the alcohol to add the requisite number of oxypropylene groups to the alkyl moiety. Since, in the above formula, x has an average value of from 0 to 4, at least one mol of propylene oxide is added to one mole of the alcohol to provide the precurser to the amine used to prepare the compounds of this invention. Preferably, x has an average value of from 0.5 to 1.5. Thus, from 1.5 to 2.5 mols of propylene oxide added to the alcohol ultimately results in the preferred compound of this invention.

The alcohols are standard items of commerce derived from any of several processes including hydrogenation of acids or esters from natural fats, the so-called "Ziegler" alcohol process, the hydroformylation of olefins, or the oxidation of paraffins. While it is preferable that the alcohol used be substantially linear in nature, some branching may be present in the alkyl portion of the molecule.

The propoxylation reaction is conducted by methods well known to those skilled in the art by reacting the alcohol with the propylene oxide in the presence of a catalyst, usually a basic material such as potassium hydroxide.

The propoxylated alcohols are reacted with ammonia using a known method of aminolysis such as, for example, that described in U.S. Patent 3,654,370 wherein the propylene oxide adduct of a polyhydric material is reacted with ammonia in the presence of a hydrogenation-dehydrogenation catalyst to form polyetherdiamines and higher amines. The preferable catalyst of the ammonolysis would be one containing nickel, copper and chromium as described for example in U.S. Patent 3,152,998. This catalyst is generally prepared by the reduction of a mixture of the oxides of nickel, copper and chromium in the presence of hydrogen at a temperature within the range of 250° to 400°C. Calculated on an oxide free basis, the catalyst contains 60 to 85 mol percent chromium. A particularly preferred catalyst composition is one containing 70 to 80 mol percent nickel, 20 to 25 mol percent copper and 1 to 5 mol percent chromium.

The ammonolysis reaction is generally conducted at a temperature of from 100°C. to 300°C. and at a pressure of 500 to 5000 psig pressure created at least in part by the presence of hydrogen. Ammonia is introduced into the reaction such that there is a minimum of one mol of ammonia per hydroxyl group to be aminated. It is preferable that an excess, usually from 10 to 30 mols ammonia per hydroxyl group, is present. The reaction can be conducted either as a batch or continuous reaction.

The aminated material, now containing internal ether groups from the reaction of the propylene oxide, is reacted with ethylene oxide to provide the improved products of this invention having shorter wetting times when used as a wetting agent which improve the reduction of surface tension of aqueous solutions. The ethylene oxide is added in such amounts to insure the reaction with both of the available amino hydrogen atoms. Preferably, the addition is made in two steps, the first step is a non-catalytic reaction conducted, under pressure, at 120 to 180°C. to react both of the amino hydrogen atoms with ethylene oxide. Subsequently, the amount of ethylene oxide desired to accomplish the results of this invention is added, utilizing a known alkoxylation catalyst such as potassium hydroxide. Once the reaction is complete, the catalyst is neutralized with an acid, such as oxalic acid, to form a solid salt which can be removed by filtration or with acids such as acetic acid which form soluble salts and are left in the product. The reaction mixture is then stripped under vacuum to leave the surface-active product of this invention.

The total ethylene oxide added to the nitrogen atom is from 2 to 20 mols per mole of aminated material. Of course, the chain lengths vary somewhat and the total number of mols of ethylene oxide is an average in the mixture. Preferably the total number of mols present on the nitrogen atom averages from 5 to 15 moles of ethylene oxide.

It is known, of course, that as more ethylene oxide is reacted with the amine, the surface tension and wetting time increases. However, surprisingly, the use of the compounds of this invention leads to lower values of surface tension and wetting time than the use of the fatty amine ethoxylates having the same number of mols of ethylene oxide added to the nitrogen atom in the molecule.

The compounds of this invention are used in the conventional way well known to those skilled in the art as components for detergents, dispersents, wetting agents, emulsifiers, and

the like, to impart improved wetting properties and surface tension lowering advantages. Further, the compounds of this invention have lowered pour points as compared with the comparable prior art materials. This invention will be further illustrated and amplified by the following examples which are offered herein for purposes of illustration and not limitation of this invention.

Example I

A stirred autoclave was charged with 256 g of amine having the structure:

$$R-(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_x-OCH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$$

where R is an alkyl group having 10-12 carbon atoms derived from Ethyl Corporation's "Epal 1012" alcohol, by propoxylating the alcohol of formula ROH followed by an ammonolysis step. The average value of x is 0.75. The autoclave was flushed with nitrogen, and heated to 140°C. Over a period of three hours and 40 minutes, 100 g. of ethylene oxide was added while the temperature was maintained at 156-162°C. After a digestion period of one hour, the autoclave was cooled and vented and the reaction mixture was stripped with nitrogen under vacuum. The recovered product contained 2.69 meg/g. of amine, 2.69 meg/g. tertiary amine and had a hydroxyl number of 289 (mg KOH/g). A total of 2 moles of ethylene oxide had been added on giving a product in which y + z = 2

Example II

Following the procedure of Example I in a larger pressure vessel, 20 lb. of the same amine as used in Example I was reacted with 6.5 lb. ethylene oxide at 145-168°C. over a total period of 5 hours 15 minutes. The recovered product, 25.9 lbs., had the following analysis: total amine = 2.71 meg/g.; tertiary amine = 2.70 meg/g.; hydroxyl number = 293; pH of 1% solution in isopropyl alcohol-water = 9.6; density = 0.9453; refractive index, n_D^{25} = 1.4591; viscosity at 25° = 72 cps. As in the product of Example I, a total of 2 moles of ethylene oxide had been added on giving a product in which y + z = 2.

Example III

A stirred pressure vessel was charged with 8 lb. of the ethoxylated alkoxypropylamine product of Example II, flushed with nitrogen, heated to 105°C. and 15 g. 50% potassium hydroxide was added. The mixture was stripped with nitrogen under vacuum, heated to 115°C., and 2.91 lb. of ethylene oxide was added over a one hour period while the temperature was maintained at 124-126°C. After an additional reaction time of 50 min., the reaction mixture was cooled to 98° and 9 g. oxalic acid in 15 ml. water was added. The reaction mixture was stripped under vacuum and filtered to yield 9.75 lb. product. The product was a five mol ethylene oxide adduct of the amine precursor and had the following analyses: hydroxyl number = 214; cloud point (1% solution) = 37.3°C.; pour point = <-20°F.; density = 0.9881, refractive index n_D^{25} = 1.4607; viscosity at 25° = 87.5 cps.

Example IV

Using the procedure of Example 3, 6 lb. of the product of Example II was reacted with 5.8 lb. ethylene oxide to give 10.6 lb. product. The product was a ten mol ethylene oxide adduct of the amine precursor and had the following analyses: total amine = 1.35 meg/g.; hydroxyl number = 147; pH (1% aqueous solution) = 9.6; cloud point = 94°C.; density = 1.02521; refractive index n_D^{25} = 1.4636; viscosity at 25° = 133 cps.

Example V

Using the procedure of Example III, 7.1 lb. of ethylene oxide was added to 4.5 lb. of the product of Example II to give 10.3 lb. of product. The product was a fifteen mol ethylene oxide adduct of the amine precurser and had the following analyses: total amine = 0.96 meg/g.; hydroxyl number = 102; density at 20°C. = 1.0546; pour point = 35°F.; refractive index n_D^{25} = 1.4657; viscosity at 25° = 190 cps.

Example VI

Using the procedure of Example III, 7.61 lb. of ethylene oxide was added to the product of Example II (3.5 lb.) to give 9.4 lb. of product. The product had the following analyses: total amine = 0.75 meg/g.; hydroxyl number = 91; pour point = 55°F.; density at 20° = 1.0645; viscosity at 25° = 219 cps.; refractive index n_D^{25} = 1.4667. A total of 18.28 moles of ethylene oxide had been added on giving a product in which $y + z$ is substantially 18.

Example VII

The following table is given to compare the products of the present invention with the ethoxylates of prior art fatty amines derived from coco oil which has an average of about 12 carbon atoms in the chain. The carbon chain length of coco oil is as follows:

Carbon-chain length	%
C_8	8
C_{10}	7
C_{12}	50
C_{14}	16
C_{16}	9
C_{18} (saturated)	5
C_{18} (unsaturated)	5

As can be seen from the following table, the products of the present invention are clearly superior, in terms of surface tension reduction and wetting properties, to the prior art fatty amines having a comparable degree of ethoxylation.

TABLE

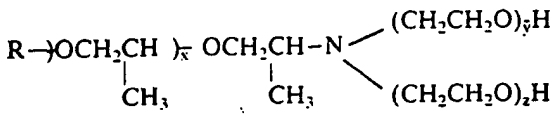
Material	Example III (5 EO)	Coco Fatty Amine C_{12} + 5 EO	Example IV (10 EO)	Coco Fatty Amine C_{12} + 10 EO	Example V (15 EO)	Coco Fatty Amine C_{12} + 15 EO
Surface tension						
1% solution	29	33[1]	32.2	38[1]	34.4	41[1]
0.1% solution	28.8	33[1]	33.3	39[1]	34.3	41[1]
0.01% solution	30.8		36.2		46.5	
Wetting times, Draves Method, sec.						
0.25% solution,						
3 g. hook	*	11.7	8	46.7	93	180
0.1% solution,						
1 g. hook	4		36.4			

*Too fast to measure.

[1]Nonionic Surfactants, M. J. Schick Ed., Marcel Dekker, Inc., New York 1967, pg. 198.

WHAT WE CLAIM IS:-

1. A surface-active agent composition of the formula:



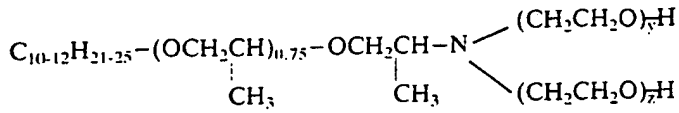
wherein R is an alkyl group containing from 8 to 18 carbon atoms; x has an average value of from 0 to 4, and y and z have an average value such that y plus z has an average value of from two to 20; provided however that neither y nor z may be zero.

2. The composition of Claim 1 wherein R is an alkyl group having from 10 to 14 carbon atoms.

3. The composition of Claim 1 wherein x has an average value of from 0.5 to 1.5.

4. The composition of Claim 1 wherein the average value of y + z is from 5 to 15.

5. Composition of the formula:



where the average value of y = z is from 5 to 15.

6. A surface-active agent composition as claimed in Claim 1 and substantially as hereinbefore described with reference to any of the Examples.

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